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RAPID AND SIMPLE METHOD FOR THE PREPARATION OF IRON NANOPARTICLES FUNCTIONALIZED WITH ALGINATE AND THEIR USE AS ADSORBENT

BY

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Abstract. In recent years, the use of iron nanoparticles in absorption processes has been considered promising alternative to traditional methods, due to the numerous advantages. The most important advantage is that iron nanoparticles can be easily functionalized with various organic compounds and thus their adsorbent performance can be improved. In this study, an easy and simple method was used for the preparation of iron nanoparticles functionalized with alginate (Fe-NPs-Alg), and the adsorbent performances of the obtained material were tested for the removal of Cu(II) ions from an aqueous solution.The batch absorption experiments were performed as a function of initial Cu(II) ions concentration and contact time, at constant initial solution pH of 4.4, adsorbent dose (2.0 g/L) and room temperature (25 ± 1°C). The adsorption experiments showed that the Cu(II) ions adsorption on Fe-NPs-Alg reaches the equilibrium in maximum 120 min, and the maximum adsorption capacity is 36.53 mg/g. The results have indicate that Fe-NPs-Alg have good adsorptive characteristics and can be used for the removal of heavy metal ions from aqueous solution.

Keywords: iron nanoparticles; alginate; functionalization; Cu(II) ions adsorption; aqueous media.

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1. Introduction

The pollution of the environment with metal ions is a major problem, which is why the researchers focused on remedying this threat, especially due to the complex problem of this phenomenon, but also from the large variety of polluting metal ions and pollution sources from which they can come from (Wang *et al.*, 2011). The accumulation of metal ions in the environment is a consequence of industrial activities, in most cases.

The discharge of industrial effluents containing heavy metal ions into aquatic environments is one of the main sources of environmental pollution. This fact significantly affects the quality of the ecosystems, which is why it has become one of the priority issues for the safety of the environment (Donmez and Aksu, 1999). Therefore it is necessary to remove heavy metal ions from industrial effluents, and this is important for both environmental protection (because heavy metal ions are non-degradable, toxic and have a tendency to accumulate in the environmental components (water, soil) they come in contact with), as well as for economic reason (because obtaining them most often involves high costs) (Shahwan, 2011).

Conventional methods used for metal ion removal have some disadvantages, such as incomplete removal of polluting metal ions, low selectivity, huge amounts of toxic waste or high energy consumption and require high cost (Febrianto *et al.*, 2009). All these disadvantages have led to the development of new methods for removing heavy metal ions from aqueous environments, which will minimize these disadvantages, a very important issue from an application point of view, for which technologically viable solutions are still being sought.

Nanoparticles are submicron particles with a diameter between 1 - 100 nm and can be obtained from organic and inorganic materials. Because the nanoparticles have high specific surface area and porous structure can be successfully used for the removal of heavy metals contaminants from industrial wastewater. Numerous such applications are described in literature for iron nanoparticles (Chen, 2005; Elsaesser *et al.*, 2010; Dong *et al.*, 2014; Ban and Subhankar, 2014).

Iron nanoparticles can be synthesized by various conventional techniques, such as condensation evaporation, sol-gel processes, combustion methods, hydrothermal processes, pyrolysis, technically and microemulsions, assisted electrochemical synthesis, wet chemical method, metal vapors, chemical reduction, gas condensation and co-precipitation (Shine, 2008; Faraji *et al.*, 2010; Shahwan, 2011). Among all of these methods, hydrothermal processes are most frequently used, at least at laboratory scale (Dong *et al.*, 2014; Wang *et al.*, 2011).

Unfortunately, not always the iron nanoparticles obtained by hydrothermal processes have good adsorptive performances for heavy metal ions from aqueous solution. This is why, various functionalization procedures have been proposed to improve their adsorptive performance (Espitia *et al*., 2012; Esakkimuthu *et al*., 2014).

In this study, iron nanoparticles functionalized with alginate were prepared by a simple method, and the adsorptive performances of the obtained material have been tested for the removal of Cu(II) ions from aqueous media. The batch absorption experiments were performed as a function of initial Cu(II) ions concentration and contact time, in optimal experimental conditions (pH 4.4; 2.0 g/L adsorbent dose, room temperature (25 ± 1°C)). The obtained results have shown that the obtained iron nanoparticles functionalized with alginate (Fe-NPs-Alg) have good adsorptive characteristics and can be used for the removal of heavy metal ions from aqueous solution.

2. Methods

2.1. Preparation of Iron Nanoparticles Functionalized with Alginate

The red marine algae (*Callithamnion corymbosum*) were collected from the Black Sea coast, in August 2016. The collected biomass was washed several times with distilled water to remove impurities and dried in air at 70°C, for 8 h. After drying, the biomass was crushed and sieved to a particle size of 1.0 – 1.5 mm and stored in desiccators for further use.

The alginate was extracted from red marine algae (*Callithamnion corymbosum*) in basic media, when 5 g red marine algae biomass have been treated with 100 mL of 1M NaOH solution for 4 h for the dissolution of sodium alginate from marine algae composition. The obtained liquid phase has been heated for 24 h at 50°C and then cooled to 10°C, using an ice bath. The obtained alginate solution was then used for the preparation of functionalized iron nanoparticles. Thus, 3.9762 g of $FeCl_2$ and 5.4061 g of $FeCl_3$ were dissolved each in 50 mL of alginate solution. The two solution were mixed, vigorously stirring for 1 h, and precipitated with 1 N NaOH solution (pH = 10-11). After precipitation, the functionalized iron nanoparticles (Fe-NPs-Alg) were filtered (using quantitative filter paper), washed with distilled water, dried in air at room temperature and kept in desiccators.

The superficial functional groups of obtained Fe-NPs-Alg adsorbent were examined by FTIR spectrometry (Bio-Rad Spectrometers (Perkin Elmer, Waltham, MA, USA), spectral-domain = 400–4000 cm^{-1}, resolution = 4 cm^{-1}, KBr pellet technique).

2.2. Adsorption Experiments

The adsorptive performances of Fe-NPs-Alg was tested for the removal of Cu(II) ions from aqueous media. Two parameters have been examined in the adsorption experiments, namely: initial Cu(II) ions concentration and contact time, in batch experiments. In all experiments, 0.05 g of each adsorbent was mixed with 25 mL of Cu(II) ions solution (12-240 mg/L), at pH 4.4, and room temperature (25 ± 1°C), at well-defined time interval (5 min-24 h). Then the two phases were filtered, and the Cu(II) ions concentration was determined with Digital Spectrophotometer S 104D (JKI, Shanghai, China) (rubeanic acid, λ= 390 nm, 1 cm glass cell, against distilled water).

The adsorption capacity (q, mg/g) and the removal percent (R, %) were calculated using the relations:

$$q = \frac{(c_0 - c) \cdot V}{m} \quad (1)$$

$$R = \frac{c_0 - c}{c_0} \cdot 100 \quad (2)$$

where: c_0 and c are the initial and equilibrium Cu(II) ions concentration in solution (mg/g); V is a measure of solution (L), and m is the mass of adsorbent used in experiments (g).

3. Results and Discussions

3.1. Preparation of iron nanoparticles functionalized with alginate

In general, the functionalization procedures of iron nanoparticles with organic compounds involve two steps (Li *et al.*, 2006; Ahmed *et al.*, 2014): (i) preparation of iron nanoparticles, which, after being washed and dried, are used in the next stage, (ii) functionalization of iron nanoparticles. In the second stage, the iron nanoparticles are mixed with a polar organic solvent (such as ethanol, methanol, acetone, etc.) and then the organic compound used for the functionalization, is added. After vigorous stirring for a certain period of time (1-6 h), the functionalized iron nanoparticles are separated by filtration or centrifugation and dried. The main disadvantages of such functionalization procedures are related to the need to use organic solvents and the long working time. To minimize these disadvantages the procedure proposed by us allows the preparation of functionalized iron nanoparticles in a single step, without using organic solvents and in a much shorter time. In Fig. 1 is presented the schematic illustration of the proposed method for the preparation of iron nanoparticles functionalized with alginate (Fe-NPs-Alg).

As can be seen from Fig. 1, the proposed method involves the dissolution of iron salts ($FeCl_2$ and $FeCl_3$) required for the preparation of iron nanoparticles, directly in the alginate solution used for functionalization. After adjusting the pH to 10-11 (1 N NaOH solution) and vigorous stirring (1 h), the precipitation of the iron nanoparticles functionalized with alginate takes place, and the obtained solid particles can then be easily separated by filtration.

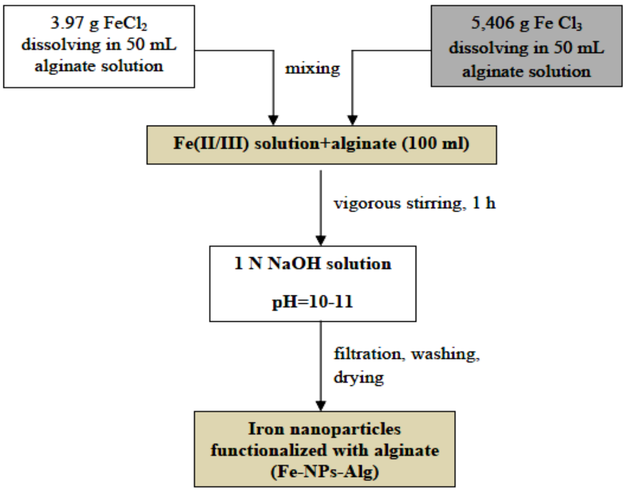

Fig. 1 – Schematic representation of the experimental methodology used for the preparation of Fe-NPs-Alg.

The obtained Fe-NPs-Alg material is washed several times with distilled water until a neutral pH, dried in air at room temperature for 3-5 days and kept in the desiccators for further use.

The presence of alginate on the surface of the iron nanoparticles and thus the presence of the superficial functional groups of Fe-NPs-Alg material was highlighted by the FTIR spectrum (Fig. 2).

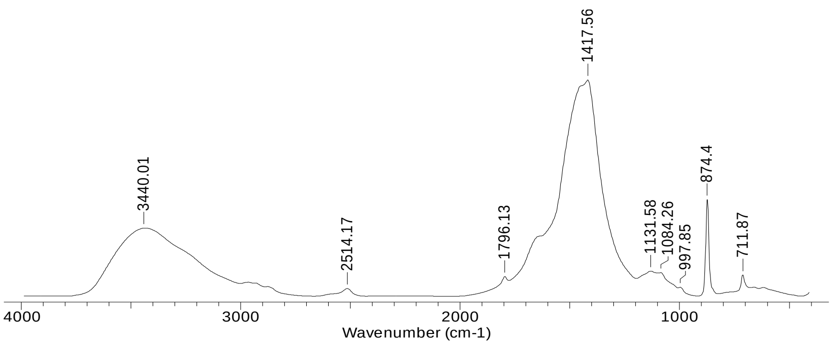

Fig. 2 – FTIR spectrum of obtained Fe-NPs-Alg.

Thus, it can be observed from Fig. 2 that Fe-NPs-Alg material has on its surface hydroxyl groups (3440 cm^{-1}), carboxyl groups (1796 cm^{-1}), carbonyl groups (1417 cm^{-1}), and etheric (1131 cm^{-1}) and esteric (1084 cm^{-1}) (Dean, 1995). In addition, the presence of the absorption band at 2514 cm^{-1} (which can be attributed to the aliphatic radicals) and the intense band from 1414 cm^{-1} indicates that most of these functional groups come from alginate and are in dissociated form, due to the use of the 1 N NOH solution in the preparation stages. On the other hand, the presence of the intense band from 874 cm^{-1}, which is characteristic to the iron nanoparticles (Bhalerao, 2014), also shows that the alginate molecules does not completely cover the formed nanoparticles. Only the ends of the alginate molecules are "trapped" inside the iron nanoparticles, leaving out the functional groups, which represent the superficial grouping of the obtained material. Therefore, the obtained Fe-NPs-Alg has on its surface a large number of functional groups and a porous structure (characteristic of nanoparticles) and can be used as adsorbent material for removing heavy metal ions from aqueous solution.

3.2. Adsorptive Characteristics of Obtained Fe-NPs-Alg Material

In order to verify whether the obtained material can be used as an effective adsorbent, adsorption studies of Cu(II) ions from aqueous solutions were performed. As it was mentioned in the Experimental section, the adsorption studies were carried out in batch systems, in optimal experimental conditions (pH = 4.4; 2.0 g adsorbent/L; room temperature), as a function of initial Cu(II) ions concentration and contact time. These two experimental parameters have been selected because they allow highlighting: (i) the efficiency of Fe-NPs-Alg material in the adsorption processes of metal ions, and (ii) the availability of the functional groups to interact with these metal ions from aqueous solution.

The experimental results obtained from the study of the influence of the initial Cu(II) concentration on the efficiency of the adsorption process using Fe-NPs-Alg adsorbent are presented in Fig. 3.

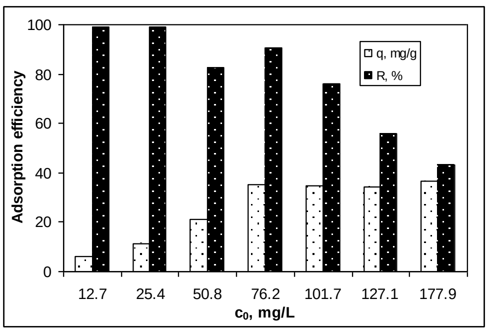

Fig. 3 – Effect of initial Cu(II) ions concentration on the efficiency of adsorption process using Fe-NPs-Alg as adsorbent.

The experimental results presented in Fig. 3 shows that the increase of the initial Cu(II) ions concentration from 12.71 to 177.90 mg/L causes the increase of the adsorption capacity (q, mg/g) from 6.14 to 36.53 mg/g. In the same concentration range of Cu(II) ions, the values of removal percent (R, %) decrease from 99.17 to 43.09 %. This is a typical variation of the values of the characteristic parameters of the adsorption process (q and R) and is mainly due to the fact that an increase of the initial metal ions concentration increases the probability of collision between metal ions and functional groups from adsorbent surface (Montazer-Rahmati *et al*., 2011). In consequence, the values of adsorption capacity (q, mg/g) will increase, while the values of removal percent (R, %), mainly because at higher metal ions concentration, the superficial functional groups are occupied, and the penetration of Cu(II) ions inside the adsorbent particles is difficult.

However, in the case of the retention of Cu(II) ions on the Fe-NPs-Alg adsorbent, the following observations should be noted:

i) at low initial concentrations ($c_0 < 25$ mg/L), the removal of Cu(II) ions is quantitative (R > 99 %) and the residual Cu(II) ions concentration in the solution separated after filtration is lower that the maximum permissible limit (NTPA 002/2005). This means that in this concentration range, Fe-NPs-Alg adsorbent can be considered an efficient adsorbent for the removal of Cu(II) ions from aqueous solution.

ii) at high initial concentrations ($c_0 > 75$ mg/L), the adsorption capacity of Fe-NPs-Alg adsorbent is almost constant (around 36 mg/g), even if the removal percent still decrease (from 90 to 43%). This indicates that on the surface of Fe-NPs-Alg adsorbent are a limited number of superficial functional groups, and once they are occupied, the efficiency of the adsorption process decreases.

The second parameters tested in the experimental adsorption studies is the contact time. The variation of the adsorption capacity of Cu(II) ions on Fe-NPs-Alg adsorbent at different values of contact time is illustrated in Fig. 4.

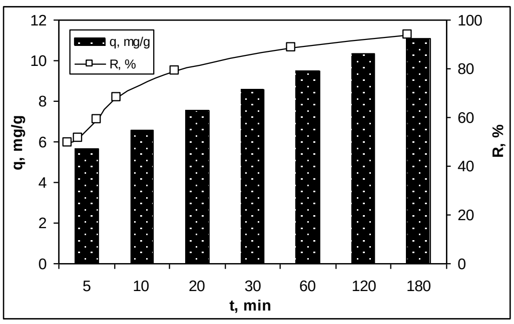

Fig. 4 – Effect of contact time on the efficiency of Cu(II) adsorption using Fe-NPs-Alg as adsorbent.

As can be seen from Fig. 4, the adsorption efficiency of Cu(II) ions on Fe-NPs-Alg adsorbent, increases with contact time, and reaches equilibrium after 120 min. In this time interval, most than 88% of initial Cu(II) ions concentration are retained, and the obtained value for the adsorption capacity is 10.35 mg/g. Under these conditions, the difference between q values obtained after 120 min and that obtained after 24 h of contact time (11.05 mg/g) is lower than 6.8%, and therefore after 120 min, the adsorption process can be considered at equilibrium. The relatively low value of the contact time required to reach equilibrium is an important argument supporting the hypothesis that the retention of Cu(II) ion on Fe-NPs-Alg adsorbent occurs predominantly by electrostatic interactions between positively charged metal ions from aqueous solution and negatively charged functional groups of alginate (Romera *et al*., 2007). But this aspect needs to be more carefully analyzed, and this will be done in a future study.

4. Conclusions

In this study, an easy and simple method was used for the preparation of iron nanoparticles functionalized with alginate (Fe-NPs-Alg), and the adsorbent performances of the obtained material were tested for the removal of Cu(II) ions from an aqueous solution. The obtained Fe-NPs-Alg has on its surface a large number of functional groups and a porous structure, and can be used as adsorbent material for removing heavy metal ions from aqueous solution. The batch absorption experiments were performed as a function of initial Cu(II) ions concentration and contact time, at constant initial solution pH of 4.4, adsorbent dose (2.0 g/L) and room temperature (25 ± 1°C). The obtained experimental results have showed that the adsorption of Cu(II) ions on Fe-NPs-Alg reaches the equilibrium in maximum 120 min, and the maximum adsorption capacity is 36.53 mg/g. All these characteristics indicate that Fe-NPs-Alg have good adsorptive performances and can be used for the removal of heavy metal ions from aqueous solution.

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METODA RAPIDĂ ȘI SIMPLĂ PENTRU PREPARAREA NANOPARTICULELOR DE FIER FUNCȚIONALIZATE CU ALGINAT ȘI UTILIZAREA LOR CA ADSORBENT

(Rezumat)

În ultimii ani, utilizarea nanoparticulelor de fier în procesele de absorbție a fost considerată o alternativă promițătoare pentru metodele tradiționale, datorită numeroaselor avantaje. Cel mai important avantaj este determinat de faptul că nanoparticulele de fier pot fi ușor funcționalizate cu diverși compuși organici și astfel performanțele lor adsorptive pot fi îmbunătățite. În acest studiu, a fost utilizată o metodă simplă și rapidă pentru prepararea nanoparticulelor de fier funcționalizate cu alginat (Fe-NPs-Alg), iar performanţele adsorbante ale materialului obținut au fost testate în procesele de îndepărtare a ionilor de Cu(II) din soluţii apoase. Experimentele de absorbție realizate în sisteme discontinui, au fost efectuate în funcție de concentrația inițială a ionilor Cu(II) și de timpul de contact, la un pH al soluției inițiale de 4,4, doza de adsorbent (2,0 g/L) și temperatura camerei (25±1°C), constante. Experimentele de adsorbție au arătat că reţinerea ionilor Cu(II) pe Fe-NPs-Alg atinge echilibrul în maxim 120 de minute, iar capacitatea maximă de adsorbție este de 36,53 mg/g. Rezultatele prezentate în acest studiu indică faptul că Fe-NPs-Alg au caracteristici bune de adsorbţie și pot fi utilizate pentru îndepărtarea ionilor de metale grele dintr-o soluție apoasă.